An X-Ray Investigation on Ternary Phases in the Ta-Me-N Systems (Me = Ti, Cr, Mn, Fe, Co, Ni)

NILS SCHÖNBERG

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

During the last three decades the nitrides of the metals Ti, V, Cr, Mn, Fe, Co, Ni have been investigated by X-ray methods, and the binary metal-nitrogen systems are well established. In most of these compounds the metal atoms are situated in a close-packed arrangement, and the nitrogen atoms are interstitially placed at the centres of octahedra of metal atoms. The general formula of the so-called normal interstitial phases are Me_2N and MeN , the former having a hexagonal close-packing (ABAB . . .) of the metal atoms, and the latter a cubic close-packing (ABCABC . . .). The structures and approximate compositions of the intermediate phases in the Ta-N system have recently been determined by the present author¹. $\text{TaN}_{0.40-0.45}$ (γ) is of the common Me_2N type. The metal atoms form a simple hexagonal lattice in the $\text{Ta}_{0.80-0.90}\text{N}$ (δ) phase. The hexagonal unit cell of the TaN (ϵ) phase contains three formula units TaN in the space-group $D_{6h}^1-P 6/m m m$ with 1Ta in 1(a) 000, 2Ta in 2(d) $1/3 2/3 1/2$; $2/3 1/3 1/2$, and 3 N in 3(f) $1/2 0 0$; $0 1/2 0$; $1/2 1/2 0$. This atomic grouping may in some respects be regarded as a mixture of the simple hexagonal stacking AA . . . and the hexagonal close-packing ABAB . . .

EXPERIMENTAL

Transition metals of fairly high purity (about 99.5 %) were used as starting materials for the preparation of intermetallic compounds of different compositions (Table 1). The finely powdered metals were carefully mixed, pressed into pastilles, and sintered (or melted) in zirconia crucibles in a high frequency vacuum induction furnace² at a temperature of about 1500° C. The alloys were then powdered in a steel mortar and placed in alumina boats in a porcelain-tube furnace. The nitriding was performed with dry ammonia at temperatures between 650° C and 950° C, the times varying between two hours and two weeks. The specimens were then cooled in ammonia to room temperature.

The phase analysis and structure determination were made from powder photographs taken with Cu-K α and Cr-K α radiation in Guinier type cameras using bent quartz and aluminium monochromators. For measurements of the high-angle reflections additional photographs were taken with Hägg-Phragmén type focussing cameras.

The nitrogen content of the samples was determined by means of the Kjeldahl method. It was not possible to obtain single crystals of any of the intermediate phases.

The sintering of different nitrides in a high frequency vacuum induction furnace at about 1350° C was not successful because of the instability of many of the nitride phases.

RESULTS

The phases observed in samples obtained by ammonia nitriding of binary alloys, together with a few ternary, at a temperature of 900° C for two days are listed in Table 1.

Ternary phases were found to exist in Ta-Me-N systems, where Me = Cr, Mn, Fe, Co, and Ni but not with Me = Ti and V. No quarternary phases were observed.

In all specimens, the dimensions of the TaN (ϵ) phase, where it existed, were invariably found to be $a = 5.185$ Å, $c = 2.908$ Å, $c/a = 0.561$ ($V = 67.70$ Å³), indicating a very small solubility of other nitrides in this phase.

Table 1. Phases obtained after ammonia nitriding of binary and ternary Ta, Me alloys (Me = Ti, V, Cr, Mn, Fe, Co, Ni) at a temperature of 900° C for 50 hours.

Alloy	Formed phases
Ta _{0.50} Ti _{0.50}	Ti(Ta)N + TaN
Ta _{0.25} Ti _{0.75}	Ti(Ta)N + TaN
Ta _{0.10} Ti _{0.90}	Ti(Ta)N + traces of TaN
Ta _{0.50} V _{0.50}	V(Ta)N + TaN
Ta _{0.25} V _{0.75}	V(Ta)N
Ta _{0.75} Cr _{0.25}	X + TaN
Ta _{0.50} Cr _{0.50}	X + traces of unknown phase
Ta _{0.25} Cr _{0.75}	Cr(Ta)N + traces of the X-phase
Ta _{0.50} Mn _{0.10}	Ta(Mn)N _{0.8} + traces of TaN
Ta _{0.75} Mn _{0.25}	Ta ₂ MnN ₄
Ta _{0.50} Mn _{0.50}	X + Ta ₂ MnN ₄
Ta _{0.25} Mn _{0.75}	X + Mn-nitrides
Ta _{0.50} Fe _{0.20}	Ta ₂ FeN ₃ + TaN
Ta _{0.47} Fe _{0.33}	Ta ₂ FeN ₃
Ta _{0.50} Fe _{0.50}	Ta ₂ FeN ₃ + Fe-nitrides
Ta _{0.50} Co _{0.20}	Ta ₂ CoN ₃ + TaN
Ta _{0.47} Co _{0.33}	Ta ₂ CoN ₃
Ta _{0.50} Co _{0.50}	Ta ₂ CoN ₃ + α -Co
Ta _{0.50} Ni _{0.20}	Ta ₂ NiN ₃ + TaN
Ta _{0.47} Ni _{0.33}	Ta ₂ NiN ₃
Ta _{0.50} Ni _{0.50}	Ta ₂ NiN ₃ + Ni
(Ta _{0.50} Cu _{0.50})	(Ta ₂ N + Cu)
Ta _{0.33} Ti _{0.33} Mn _{0.33}	Ti(Ta)N + Ta ₂ MnN ₄ + x + η -MnN
Ta _{0.33} Ti _{0.33} Co _{0.33}	Ti(Ta)N + (Ti, Ta) ₂ N + α -Co
Ta _{0.33} V _{0.33} Cr _{0.33}	(V, Cr, Ta)N + x + y *
Ta _{0.33} V _{0.33} Co _{0.33}	V(Ta)N + TaN + α -Co
Ta _{0.33} V _{0.33} Ni _{0.33}	V(Ta)N + TaN + Ni
Ta _{0.33} Cr _{0.33} Co _{0.33}	Cr(Ta)N + x + α -Co
Ta _{0.33} Mn _{0.33} Co _{0.33}	Ta ₂ MnN ₄ + Mn-nitrides + α -Co
Ta _{0.33} Fe _{0.33} Co _{0.33}	Ta ₂ (Fe, Co)N ₃ + Fe-nitrides + α -Co
Ta _{0.33} Co _{0.33} Ni _{0.33}	Ta ₂ (Co, Ni)N ₃ + α -Co + Ni
Ta _{0.47} Fe _{0.11} Co _{0.11} Ni _{0.11}	Ta ₂ (Fe, Co, Ni)N ₃

* The phase designated by y was found to have a tetragonal unit cell with the dimensions $a = 4.244$ Å, $c = 4.120$ Å, $c/a = 0.971$. As the corresponding alloy was contaminated by a small amount of oxygen this phase is most likely an oxide or an oxide-nitride.

The Ta-Ti-N system

No ternary phase seems to exist. The solubility of Ta in TiN is probably about 10 atom %. For pure TiN (50 atom % of N) the cube edge was found to be 4.238 Å, and for a nitride of the approximate composition ($\text{Ti}_{0.90}\text{Ta}_{0.10}$) N the cube edge was 4.247 Å. This compound was not pure, however, but contained traces of TaN.

The Ta-V-N system

Only phases which were solid solutions in binary phases were found. The VN phase dissolves approximately 25 atom % of Ta, the cube edge increasing from $a = 4.169$ Å ($\text{VN}_{1.00}$) to $a = 4.291$ Å.

The Ta-Cr-N system

One ternary phase was found to exist (designated by X in Table 1). As it was not possible to obtain it in a pure state the composition is unknown. The pattern indicates a complicated structure. The lattice constant of the CrN phase increases from $a = 4.149$ Å ($\text{CrN}_{1.00}$) to $a = 4.293$ Å, the latter value being obtained at the point of the maximum solubility of Ta in the cubic close-packed lattice (about 25 atom %).

The Ta-Mn-N system

Two ternary phases were found to exist, viz. one phase isomorphous with the corresponding Ta-Cr-N phase (X in Table 1) and one phase with a composition close to the formula Ta_3MnN_4 . The structure of the latter has been determined. No solubility of Ta in $\text{MnN}_{0.61-0.63}$ (η phase) or of Mn in ϵ -TaN could be detected. But Mn atoms can replace about 10 % of the Ta atoms in δ -TaN, causing an expansion along the a axis of the simple hexagonal unit cell, and a contraction along the c axis. For $\text{TaN}_{0.80-0.90}$ (δ phase) the following dimensions were found: $a = 2.925-2.938$ Å, $c = 2.876-2.883$ Å, $c/a = 0.983-0.981$ ($V = 21.31-21.55$ Å³). The dimensions of the δ phase in a sample of the composition $(\text{Ta}_{0.90}\text{Mn}_{0.80})\text{N}_{0.84}$ were found to be $a = 3.057$ Å, $c = 2.819$ Å, $c/a = 0.922$ ($V = 22.81$ Å³). This specimen contained traces of TaN as an impurity. It is remarkable that the substitution of Mn atoms for Ta atoms causes an increase of the unit volume in spite of the fact that the atomic radius for Mn is smaller than that for Ta.

The structure of the Ta_3MnN_4 phase

Powder photographs of the Ta_3MnN_4 phase showed lines with $\sin^2\theta$ values closely proportional to rather small integers. In spite of this, a cubic symmetry was improbable because of a great number of absent reflections. If small amounts of titanium were introduced into the lattice, the phase $(\text{Ta}_{0.9}\text{Ti}_{0.1})_3\text{MnN}_4$ was found to be homogeneous and slightly deformed, compared with the titanium free phase. This deformation was large enough to make a unit cell determination possible from the $\sin^2\theta$ values of the diffraction lines. The phase was found to have hexagonal symmetry with the following dimensions:

$$\begin{array}{ll} (\text{Ta}_{0.9}\text{Ti}_{0.1})_3\text{MnN}_4 & a = 3.027 \text{ Å}, c = 10.57 \text{ Å}, c/a = 3.492 (V = 83.87 \text{ Å}^3) \\ \text{Ta}_3\text{MnN}_4 & a = 3.023 \text{ Å}, c = 10.49 \text{ Å}, c/a = 3.470 (V = 82.99 \text{ Å}^3). \end{array}$$

The fact that c/a is very close to the value $2\sqrt{3} = 3.464$ for the phase containing only the metals Ta and Mn explains the above-mentioned difficulty in interpreting the powder photographs of this phase.

The nitrogen content is probably slightly lower than is indicated by the formula Ta_3MnN_4 . Analyses corresponded to the composition $\text{Ta}_3\text{MnN}_{3.85}$. This formula is not quite certain, however, as the samples may have contained other phases not discernible in the powder photographs. The density calculated for a unit cell content of three Ta atoms and one Mn atom is 13.04. The observed value was 12.4.

Reflections with $h-k = 3n$ and $l = 2n$ are absent in the diffraction pattern. This absence is characteristic of atomic positions in the space-groups $D_{6h}^4-P 6_3/mmc$, $C_{6v}^4-P 6_3 mc$, $D_{3h}^4-P\bar{6} 2c$, $C_{6h}^2-P 6_3/m$, $C_{6d}^6-P 6_3$, $D_{3d}^2-P \bar{3} 1c$ and $C_{3v}^4-P 3 1c$. From space considerations, the metal atoms must be in a close-packed arrangement. The only possible grouping in this case is a packing sequence designated by ABACABAC..., i. e. the mixture of the hexagonal close-packing ABAB... and the cubic close-packing ABCABC..., which is characteristic of the position of the anions in topaz. If the metal atoms are assumed to be distributed at random, the calculated and observed intensity values differ to some extent, especially for comparatively small diffraction angles. For this reason the manganese atoms have been assumed to have ordered positions. The agreement between calculated and observed intensities is good for an ordered distribution with the following atomic positions in the

Table 2. Calculated and observed intensities for Ta_3MnN_4 .

hkl	$I_{\text{calc.}}$	$I_{\text{obs.}}$	hkl	$I_{\text{calc.}}$	$I_{\text{obs.}}$
002	20	25	0 0 10	1	0
004	68	70	2 0 6	28	25
100	1		1 1 8	58	50
101	102	100	2 1 0	0	0
102	144	150	2 0 7	17	50
103	64	70	2 1 1	33	
104	1	0	1 0 10	25	25
006	1	0	2 1 2	50	50
105	39	35	2 1 3	30	25
110	62	70	2 0 8	0	0
106	53	70	2 1 4	1	0
112	8		1 0 11	14	15
008	18	15	2 1 5	27	25
114	106	100	0 0 12	7	10
200	0		3 0 0	22	25
107	31	70	2 0 9	13	15
201	31		1 1 10	3	0
202	42	35	2 1 6	0	0
203	26	25	3 0 2	3	0
108	0	0	1 0 12	0	0
204	0	0	3 0 4	53	50
116	4	0	2 1 7	32	25
205	20	15	2 0 10	28	25
109	18	15	2 1 8	0	0

Table 3. Interatomic distances in Ta_3MnN_4 .

Atom	Surrounding atoms	Interatomic distance, Å
(Ta, Mn) in 2(a)	6 (Ta, Mn) 6 Ta 6 N	3.02 3.15 2.18
Ta in 2(d)	6 Ta 6 (Ta, Mn) 6 N	3.02 3.15 2.18
N in 4(f)	3 (Ta, Mn) 3 Ta 1 N	2.18 2.18 2.62

space-group $D_{6h}^{4}-P$ $6_3/m\ m\ c$; 1 Ta + 1Mn in 2(a) 000; 001/2 and 2 Ta in 2(d) $1/3\ 2/3\ 3/4$; $2/3\ 1/3\ 1/4$. The corresponding intensity values are listed in Table 2. The most likely positions of the nitrogen atoms are 4(f) $1/3, 2/3, z; 2/3, 1/3\ z; 2/3\ 1/3\ 1/2 + z; 1/3\ 2/3\ 1/2 - z \sim 1/8$. The parameter z probably has a value slightly different from $1/8$, because the nitrogen atoms are octahedrally surrounded by metal atoms of two different kinds ($1\frac{1}{2}$ Ta + $1\frac{1}{2}$ Mn in 2(a) and 3Ta in 2(d)).

Interatomic distances are listed in Table 3, under the assumption that $z_{(f)} = 1/8$.

The Ta-Fe-N, Ta-Co-N and Ta-Ni-N systems

The Ta-Me-N systems with Me = Fe, Co and Ni are very similar. No solubility of Ta in Fe-nitrides was observed. One hexagonal ternary phase, closely related to the Ta_3MnN_4 phase and with a composition close to the formula $Ta_2MeN_{2.5}$ (Me = Fe, Co, Ni), was found in the three systems. In this phase the metals Fe, Co and Ni can replace each other in all proportions. No other ternary phase seems to exist. The unit cell dimensions as well as the calculated and observed densities are listed in Table 4.

A comparison of the diffraction patterns of the phases Ta_3MnN_4 and $Ta_2MeN_{2.5}$ (Me = Fe, Co, Ni) showed such a similarity that the metal atoms

Table 4. Unit cell dimensions, calculated and observed densities for $Ta_2MeN_{2.5}$ (Me = Fe, Co, Ni).

Phase	a , Å	c , Å	c/a	Density	
				calc.	obs.
$Ta_2FeN_{2.60}$	5.156	10.31	2.000	12.71	11.9
$Ta_2CoN_{2.50}$	5.161	10.30	1.996	12.74	12.3
$Ta_2NiN_{2.45}$	5.168	10.36	2.005	12.60	12.2
$Ta_2(Fe_{0.33}Co_{0.33}Ni_{0.33})N_{2.50}$	5.162	10.33	2.001	12.67	12.1

Table 5. Calculated and observed intensities for $Ta_2NiN_{2.45}$.

$h k l$	$I_{calc.}$	I_{obs}	$h k l$	$I_{calc.}$	I_{obs}
002	24	25	214	4	5
100	12	10	206	2	0
102	14	15	008	14	15
004	58	60	304	86	100
110	0		220	0	
111	92	100	117	24	25
112	116	100	221	24	25
104	4	5	222	34	40
200	2		108	2	0
113	57	60	310	2	0
202	3	5	223	23	25
114	0	0	216	3	0
006	2	0	312	3	0
204	2	5	118	0	0
210	2		224	0	0
115	34	40	306	0	0
106	2	0	208	1	0
212	5	5	314	2	0
300	53	60	400	1	
116	46	40	225	17	15
302	8	10	402	1	0

must have the same packing sequence (ABACABAC . . .) in both compounds. A series of comparatively weak extra reflections seems to indicate that the Me atoms possess an ordered distribution. The intensities of these superlattice lines commonly grow weaker at increasing diffraction angles, and this is characteristic of ordered atomic positions, not of a displacement of the atomic positions from the "ideal" lattice points. The c axes of the two phases have almost the same values, and the a axis of the latter phase is approximately $\sqrt{3}$ times greater than that of the Ta_3MnN_4 phase. The $00l$ reflections with $l = 2n + 1$ and the $h k l$ reflections with $h \neq k$ and $l = 2n + 1$ are absent in the diffraction pattern. A systematic interpretation of the possible metal atom positions resulted in the following atomic arrangement in the space-group D_{3h}^3 — $P \bar{6} m 2$:

- 2 Ta in $2(c)$ $0 0 z$; $0 0 z$ with $z = 1/4$
- 3 Ta in $3(f)$ $x 0 0$; $0 x 0$; $\bar{x} \bar{x} 0$ with $x = 1/3$
- 3 Ta in $3(g)$ $x 0 1/2$; $0 x 1/2$; $\bar{x} \bar{x} 1/2$ with $x = 2/3$
- 4 Me in $4(h)$ $1/3 2/3 z$; $1/3 2/3 \bar{z}$; $2/3 1/3 z$; $2/3 1/3 \bar{z}$ with $z = 1/4$

The calculated and observed intensities for the $Ta_2NiN_{2.45}$ phase are compared in Table 5.

It is not possible to determine the positions of the nitrogen atoms from X-ray data, but they are most likely to be situated at the centres of metal atom octahedra. Furthermore they are probably placed in the octahedral "holes" having the highest N-Ta coordination numbers.

Table 6. Interatomic distances in $Ta_2MeN_{2.50}$
($Me = Fe_{0.33}Co_{0.33}Ni_{0.33}$).

Atom	Surrounding atoms	Interatomic distance, Å
Ta in 2(e)	3 Ta in 3(f)	3.10
	3 Ta in 3(g)	3.10
	6 Me in 4(h)	2.98
Ta in 3(f)	1 Ta in 2(e)	3.10
	6 Ta in 3(f)	2.98
	3 Ta in 3(g)	3.10
	2 Me in 4(h)	3.10
Ta in 3(g)	1 Ta in 2(e)	3.10
	3 Ta in 3(f)	3.10
	6 Ta in 3(g)	2.98
	2 Me in 4(h)	3.10
Me in 4(h)	3 Ta in 2(e)	3.10
	3 Ta in 3(f)	2.98
	3 Ta in 3(g)	3.10
	3 Me in 4(h)	2.98

The intermetallic distances in the $Ta_2(Fe_{0.33}Co_{0.33}Ni_{0.33})N_{2.50}$ phase are recorded in Table 6.

The homogeneity ranges of the compounds Ta_3MnN_4 and $Ta_2MeN_{2.5}$ ($Me = Fe, Co, Ni$) seem to be rather narrow, as indicated by the very small variations of the unit cell dimensions.

SUMMARY

Binary and ternary Ta, Me alloys ($Me = Ti, V, Cr, Mn, Fe, Co, Ni$) have been nitrided with dry ammonia at temperatures varying between 650° C and 950° C. The following ternary nitride phases have been found to exist: Ta_3MnN_4 is hexagonal with four metal atoms in the unit cell. The space-group is $D_{6h}^{4}-P6_3/m\ m\ c$. $Ta_2MeN_{2.5}$ ($Me = Fe, Co, Ni$) has a similar structure but shows a superstructure containing twelve metal atoms in the cell. The space-group is $D_{3h}^3-P\ 6\ m\ 2$. The metals Fe, Co and Ni can replace each other in all proportions.

The metal atoms in the phases Ta_3MnN_4 and $Ta_2(Fe, Co, Ni)N_{2.5}$ occupy a close-packed arrangement designated by the sequence ABACABAC...

$(Ta, Cr)N_x$ and $(Ta, Mn)N_x$ with the ratios Ta : Cr and Ta : Mn probably close to unity are isomorphous, but the structure and composition are unknown.

No solubility of Me nitrides in TaN (ϵ phase) has been detected. Up to about 10 % of the Ta atoms in TaN_{0.80-0.90} (δ phase) can be replaced by Mn atoms, thus causing a comparatively strong deformation of the simple hexagonal lattice. The TiN, VN and CrN phases of NaCl type have been found to

form solid solutions with the TaN phase up to the approximate limits 10, 25 and 25 atom % of TaN respectively. No solubility of Ta in the most nitrogen-rich nitrides of Mn and Fe has been observed.

The author wishes to thank Professor G. Hägg for his continued interest throughout the course of the work. The investigation was supported by a grant from *Statens Tekniska Forskningsråd*, which is gratefully acknowledged. I also wish to thank Mrs. U. Schönberg and Mr. S. Hedling for valuable help with preparation of the samples.

REFERENCES

1. Schönberg, N. *Acta Chem. Scand.* 8 (1954) 199.
2. Kiessling, R. *Jernkontorets Ann.* 132 (1948) 237.

Received November 5, 1953.